Renewable and Sustainable Energy Reviews 16 (2012) 3401–3408

Contents lists available at SciVerse ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A critical review on corrosion of compression ignition (CI) engine parts by biodiesel and biodiesel blends and its inhibition

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ARTICLE INFO

Article history:
Received 23 May 2011
Received in revised form 16 February 2012
Accepted 18 February 2012
Available online 30 March 2012

Keywords:
Corrosion
Static immersion
Stainless steel
Aluminum
Copper

ABSTRACT

This paper reviews the effects of corrosion on the engine parts that come in contact with a newly developed biodiesel fuel and its petrodiesel blend. Copper, aluminum, copper alloys (bronze), and elastomers caused significant levels of corrosiveness in biodiesel and biodiesel blend as opposed to low corrosion with petrodiesel. Specimens of stainless steel showed significant resistance to corrosion in biodiesel samples as compared to copper, aluminum, and copper alloys, but the level of corrosion was still higher than that in petrodiesel. Common methods adopted for measurement of corrosion include weight loss through static emersion tests, and electrochemical techniques by electrochemical impedance spectroscopy or on Potentiostat/Galvanostat. The surfaces of the specific metal strips were analyzed by optical, scanning electron, and atomic force microscopy, revealing the nature and extent of corrosion. Fourier Transform Infrared Spectroscopy revealed formation of secondary product due to degradation, and X-ray diffractometer revealed formation of a new phase in the metal strips exposed to biodiesel and its blend with mineral diesel. Biodiesel seemed to degrade due to auto-oxidation and presence of moisture to secondary products that enhanced the corrosion rate. The problem related to the use of non-compatible materials as engine parts for biodiesel-run vehicles is dual in nature. The engine part in contact with the fuel is corroded as a result of fuel degradation, causing the fuel to go further off-specification.

Contents

1. Introduction

The use of biodiesel as an alternative fuel in compression ignition (CI) engines instead of petrodiesel (also known as 'mineral diesel', but hereafter referred to as 'diesel') has advantages as well as disadvantages. One of the advantages of using biodiesel as a fuel is its high cetane number and absence of sulfur and aromatics. Among the disadvantages is its low fuel density in comparison to mineral diesel, which requires a higher amount of fuel to achieve the same power to drive the engine [1]. Until now, CI engines were suited only for a low-ratio blend of biodiesel with diesel because of corrosion. Corrosion is the disintegration of a material as it reacts with other materials with which it comes into contact. According to Nernst's theory, all metals have a tendency to pass into solution. However, the extent of corrosion varies for metal ions depending on its oxidation potential and various prevailing conditions

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doi:10.1016/j.rser.2012.02.042

(temperature, water content, etc.) in the fuel. Metal ions, when present in fuel, can cause corrosion [2]. Jung et al. [1] reported that the absence of sulfur is supposed to reduce the corrosion in the biodiesel fuel container. Hence, recently, corrosion aspect of biodiesel as fuel has been tested by researchers for its viability in CI engines. Biodiesel is generally prepared from acid or alkali catalysts that are either homogeneous or heterogeneous [3]. Homogeneous acid catalysts, such as sulfuric acid, which are generally used for acid esterification, and impart corrosive nature to biodiesel fuel [4]. This is generally overcome by using solid acid catalysts which are easily separated from biodiesel and hence do not make the fuel corrosive [5–7]. Biodiesel also ought to be of high purity for its compatibility in CI engines. Therefore, incomplete conversion or inadequate purification (by water washing or other means) may result in impurities such as glycerol, free fatty acids, alcohol, and catalyst, causing deposits in the engine, corrosion, and ultimately failure of the fuel [8]. Biodiesel has a good lubricity and hence, it has a higher tendency as compared to mineral diesel to dissolve the metallic parts in the fuel. Thus, the study of corrosion with biodiesel as fuel and search for corrosion inhibitors becomes an important aspect for the enhanced endurance of biodiesel as a fuel in the compression ignition engine. An excellent review on the compatibility of automotive materials in biodiesel has been done by Haseeb et al. [9]. Diesel engine components are made from a variety of metals, non-metals, and elastomers. The main parts of the engine/vehicle that come in contact with fuel are fuel tank, fuel feed pump, fuel lines, fuel filter, fuel pump, fuel injector cylinder, piston assembly, and exhaust system. These engine/vehicle parts are made of metallic (i.e., steel, stainless steel, copper, aluminum, copper-based alloy, aluminum-based alloy, iron-based alloy, gray-cast iron, special-cast iron, cast aluminum, forged aluminum, sand-cast aluminum, die-cast aluminum, and aluminum fiber) and non-metallic materials (i.e., elastomer, plastics, paint, coating, cork, rubber, ceramic fiber, and even paper). The fuel comes in contact with the various engine parts and its accessories at varying temperature, velocity, load, sliding, and physical state. It has been found that either the impurities in biodiesel or the deterioration of biodiesel through oxidation enhances the corrosiveness of the fuel.

2. Corrosion behavior of metal and alloys in biodiesel

Currently, the level of corrosion in biodiesel fuel is specified by the 'copper strip corrosion test' and determined by ASTM D 93 specifications [10]. A polished copper strip is immersed in a specified volume of biodiesel for a specific time and temperature. The copper strip is then removed and washed. The color of the strip is then assessed as per the ASTM standard [11]. However, the 'copper strip corrosion test' provides limited information with respect to corrosiveness as it measures the level of corrosion that will occur when copper is present as metal. Corrosion in engine parts that are made of metals, alloys, and elastomers on contact with biodiesel occur due to the chemical composition of biodiesel that is comprised of unsaturated molecules that easily undergo oxidation. Factors that influence the performance and engine durability of a CI engine run on B0 (100% pure or 'neat' diesel) or a biodiesel blend are presence of oxygen in the functional groups (moieties), free fatty acids, degree of unsaturation, and hygroscopic nature (ability to attract and hold water) of the biodiesel [12]. The level of corrosion also depends on the type of alloy in contact with biodiesel fuel. In general, copper alloys have been found to be more corrosive than the ferrous alloys [12]. Apart from biodiesel, corrosion also occurs in engines operating on ethanol. Agarwal [13] reported corrosion in engine carburetors exposed to ethanol by three ways: general corrosion, dry corrosion, and wet corrosion. General corrosion results from ionic impurities such as chloride ions and acetic acid. Dry corrosion results from polarity of the molecule. Wet corrosion arises due to azeotropic water and oxidizes various metals [13]. In biodiesel-run engines, a high chrome stainless steel has been used to make oil nozzles and was found to be resistant to corrosion when exposed to biodiesel. The oil burner filter components made of copper and copper alloys were found to corrode in biodiesel, resulting in the fuel being contaminated with copper ions. The copper content increased from 0.1 to 21 ppm after 2 h contact with the fuel when analyzed on Inductively Coupled Plasma (ICP). Corrosion was observed on the bronze filter incorporated in the oil nozzle after 10 h operation using biodiesel at 70 °C. Pitting corrosion was also observed after several hours of operation with biodiesel fuel [14].

Geller et al. [15] reported that copper and brass are prone to corrosion as observed by weight loss through pitting and deposits covering the surface. Corrosion of steel, however, is not very clear and data differ [15]. Steel is an alloy comprised mostly of iron and has a carbon content ranging from 0.2 to 2.1% by weight. The carbon content in the steel could be a reason for its high resistance to corrosion due to the fact that carbon has a high corrosion resistance [16]. Steel, until now, has been found to show high resistance to corrosion in biodiesel blends as evidenced from electrochemical impedance spectroscopy (EIS). However, Prieto et al. [17] reported that biodiesel is more conductive electrically compared to gasoline and diesel and may cause galvanic metal corrosion in steel. Corrosion of metal and metal alloys varies with feedstock used for synthesis of biodiesel. This is due to differences in the chemical composition of the feedstock that show various degrees of corrosiveness. Maru et al. [18] tested strips of structural carbon steel (CS) and high density polyethylene (HDPE) exposed to soybean biodiesel, sunflower biodiesel, and diesel using static emersion tests (SET), observing weight loss, and observing the surface by optical, scanning electron, and atomic force microscopy. The time span of the test was between 60 and 115 days. Although the weight of the CS strips did not change with exposure to biodiesel for 60 days, the soybean biodiesel was found to be more compatible with carbon steel than sunflower biodiesel and even diesel. The weight loss that occurred in carbon steel after 115 days was quite low (around 10^{-5} g) and only slightly higher in biodiesel. The Fourier Transform Infra Red (FTIR) Spectroscopy spectra revealed the formation of secondary products due to degradation of the fuel. The C=O peak was broadened and hydroxyl peaks sharpened with time (Fig. 1). Degradation of fuel was also observed in diesel, which has been attributed to its sulfur content, resulting in the formation of iron sulfide. In the HDPE strip exposed to biodiesel and diesel, a gain in weight and discoloration was observed. The gain in weight occurred during the first 75 days and then remained constant.

Corrosion becomes an important aspect in usage of biodiesel fuel because many of the engine parts are composed of metals such as aluminum, copper and its alloys, and stainless steel [19] that may be prone to corrosion. Percent aluminum in engine components includes piston (100%), cylinder heads (70%), and engine blocks (19%). Pumps and injectors are often composed of copper and its alloys. Parts composed of stainless steel include fuel filter, valve bodies, nozzle, and pump ring [20,21]. Fuel degradation varies with the specific metal used. Based on the observation that biodiesel degrades through moisture absorption, auto-oxidation, and microbial attack during storage, Fazal et al. [22] tested corrosion of aluminum, copper, and stainless steel in petrodiesel and palm biodiesel. The static immersion test conducted on B100 and diesel was done at 80 °C for 600 and 1200 h and an agitation rate of 250 rpm. The corrosion rate in copper, aluminum, and carbon steel has been found to be 0.586, 0.202, and 0.015 mils per year (mpy), respectively in palm biodiesel. In diesel, the rate of corrosion was less and found to be less than 0.3 mpy for copper, less than 0.15 mpy for aluminum, and was almost the same for

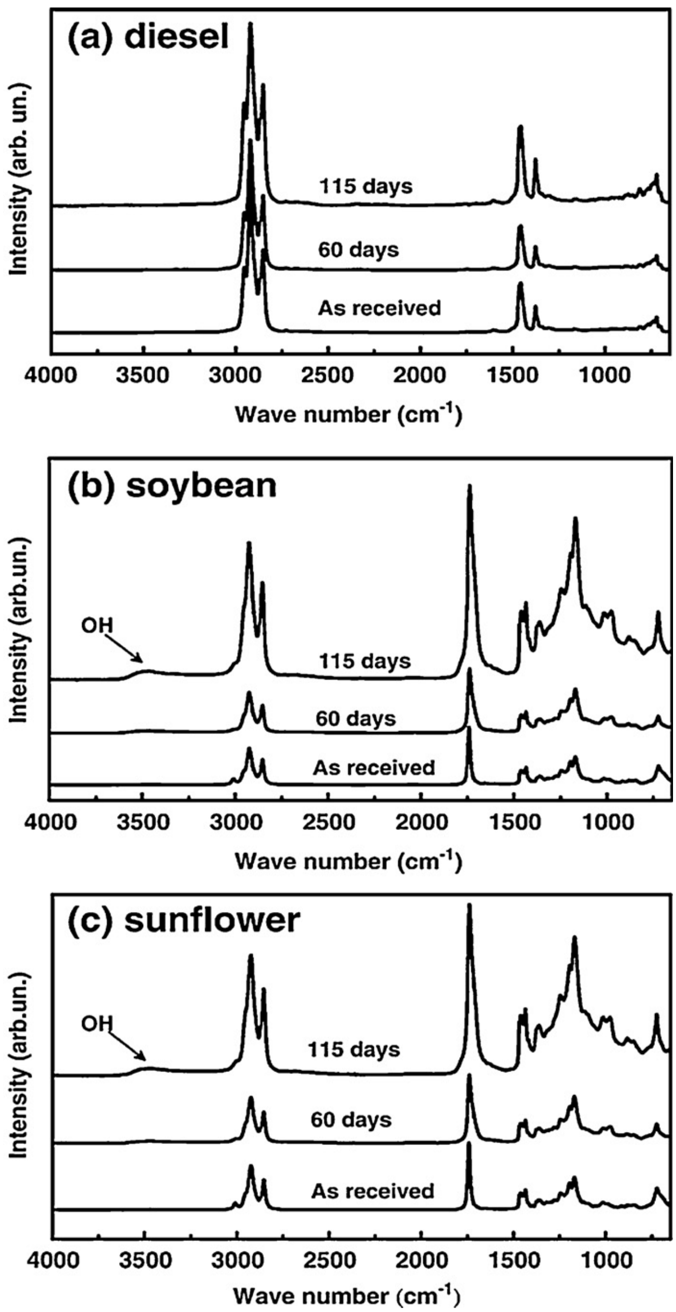


Fig. 1. FT-IR spectra of fluids before and after immersion tests. (a) Diesel; (b) soybean; (c) sunflower [18].

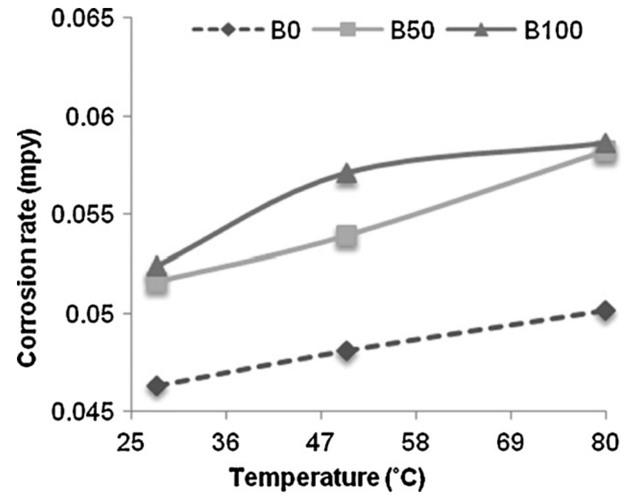


Fig. 2. Corrosion rate of mild steel after exposure to diesel (B0), B50, and B100 for 1200 h at 27, 50, and 80 °C [26].

carbon steel (0.015 mpy) [22]. In an earlier study, Haseeb et al. [23] reported the rate of corrosion to be only 0.053 mpy for copper strips at 60 °C. The enhanced rate of corrosion has been attributed to higher temperature and to the agitation of metal specimen in the fluid provided during the test [24,25]. In a recent study, Fazal et al. [26] tested the effect of corrosion on mild steel dipped in biodiesel and diesel at temperatures of 27, 50, and 80 °C. Corrosion rate increased with increasing temperature in the diesel (B0) and biodiesel, especially B50 and B100 (Fig. 2). The study of surface morphology of the test coupons suggested that the depth attack was more prominent with metal surfaces exposed to biodiesel than those exposed to diesel. Elemental analysis of the metal samples also revealed presence of oxygen on their surfaces, which increased at higher temperature, indicating oxidation of the metal surface. X-ray diffraction (XRD) analysis revealed two phases in diesel exposed metal: $Fe(OH)_3$ and Fe_2O_3. In the biodiesel-exposed metal, a new, third, $Fe_2O_2CO_3$ phase was observed in addition to $Fe(OH)_3$ and Fe_2O_3. The formation of the $Fe_2O_2CO_3$ phase has been attributed to absorption of water, oxygen, and carbon dioxide from the atmosphere.

The surface morphology of copper and aluminum strips showed a higher pitting corrosion value for biodiesel (80% and 18%, respectfully) compared to diesel (54% and 10%, respectfully). Stainless steel, however, did not show any change on its surface exposure to biodiesel [22]. The mechanism of pitting corrosion has been proposed by Mankowski et al. [27] who stated that copper interacts with atmospheric oxygen to form $CuO/CuCO_3$ in the outer layer, followed by Cu_2O in the inner layer. The same mechanism occurs in biodiesel that is rich in oxygen (approximately 11% elemental oxygen). Fazal et al. [22] found that biodiesel exposed to the various metal strips for 1200 h at 80 °C changed color due to formation of metal oxide. While copper carbonate yielded a pale green color in biodiesel, red colored cuprite oxide was dominant in diesel. Biodiesel was exposed to metal and heated with and without copper. Several new products (i.e., acids, short chain esters, and ketones) were formed with and without copper. The biodiesel exposed to copper resulted in formation of some new products such as 9-octadecenoic acid, octanoic acid, nonanoic acid, hexadecanoic acid, and 9-octadecanoic acid. The drawbacks of corrosion are dual in nature as the change in fuel composition due to corrosion results in degradation of fuel properties of the biodiesel. Copper ions in biodiesel were also confirmed by analysis with Inductively Coupled Plasma. The 'Total Acid Number' (TAN) of biodiesel, an important criterion of biodiesel as fuel, was off-specification after 1200 h of exposure to biodiesel, although no effect on TAN was observed in diesel. This was attributed to the catalytic activity of copper enhancing oxidation of the biodiesel. Although there was no water initially in either diesel or biodiesel, water was observed after the static immersion test. This water gets condensed on the metal surface and promoted the rate of corrosion. Water elicited microbial growth and corroded the fuel system components [28,29]. Water can also cause hydrolysis of biodiesel that is composed of esters to fatty acids, furthering corrosion [30]. The water content in biodiesel can convert the fatty acid alkyl esters (biodiesel) to fatty acids through a reversible reaction. The oxidative behavior of biodiesel enhances corrosion and wear of engine parts in contact with biodiesel [31].

Ballote et al. [32] used electrochemical techniques to determine the effect of corrosion in biodiesel samples exposed to aluminum

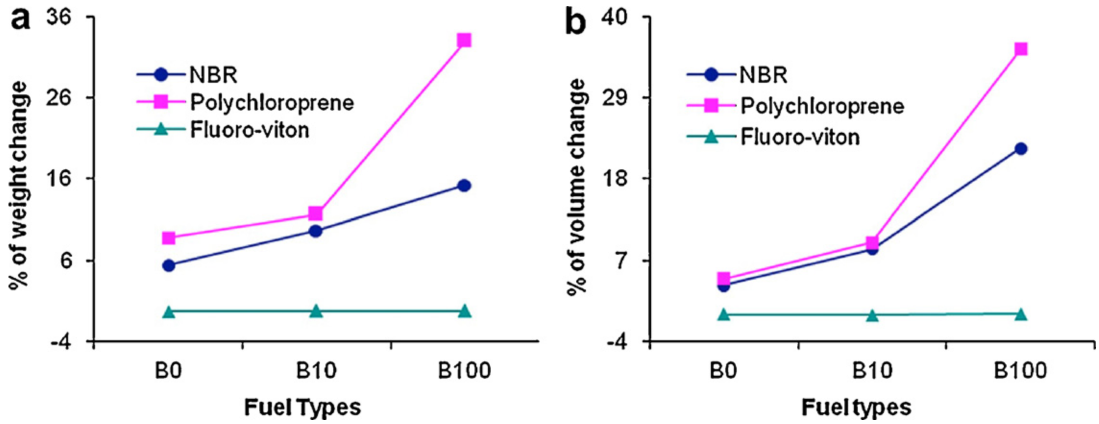


Fig. 3. Changes in: (a) weight and (b) volume of different elastomers after immersion at room temperature for 500 h [36].

during different stages of washing. The corrosion process occurred in the same manner as if aluminum was exposed to aqueous or ethanol alkaline solution. The electrochemical measurements were done by Potentiostat/Galvanostat in a 3 electrode cell. During the initial wash, the open circuit potential (E_{ocp}) showed a high negative value (−600 mV), which might have occurred due to reaction of aluminum with biodiesel. Repeated washing of biodiesel by water resulted in a positive of E_{ocp} value, which was attributed to the use of potassium hydroxide or sodium hydroxide as homogeneous catalyst which forms $Al(OH)_3$ as a passive layer. The corrosion potential (E_{corr}) was negative (below −500 mV) through six washing cycles, but increased to −50 mV after the seventh wash cycle. The corrosion current density also decreased with the number of wash cycles (from 10 nA/cm^2 to 0.10 nA/cm^2).

Kaul et al. [33] demonstrated varying rates of corrosion for aluminum strips on several feedstocks. Corrosion rates for aluminum exposed to biodiesel produced from *Jatropha curcas* (Jatropha), *Pongamia pinnata* (Karanja), *Madhuca indica* (Mahua), and *Salvadora oleoides* (Salvadora) were 0.0784, 0.0065, 0.1329, and 0.1988 mpy, respectively. Presence of fluorine can restrain swelling in the elastomers [34,35]. Kaul et al. [33] did a static immersion test (SIT) on the diesel piston liner and piston metal that came into contact with the biodiesel fuel. The SIT was conducted for 300 days at room temperature, which varied between 15 and 40 °C, and corrosion rate (mpy) and penetration (mdd) were determined. Weight losses resulting from corrosion in the piston liner exposed to Salvadora, Jatropha, Karanja, and Mahua biodiesel were 6.1, 3.6, 0.3, and 0.3 mg, respectively. A high weight loss of 2.1 mg was also observed in piston metal exposed to Salvadora biodiesel, followed decreasingly by Jatropha biodiesel (0.2 mg), then Karanja and Mahua biodiesel (0.1 mg). Corrosion rate and penetration were high in Salvadora and Jatropha biodiesel. An increase in Total Acid Number due to oxidation of the fuel was observed with Jatropha, Karanja, and Mahua, which led to increased corrosion. With Salvadora, however, the increase in corrosion was attributed to presence of a high concentration (1600 ppm) of sulfur. Although they reported that the extent of corrosion was within the permissible limits and no gum formation was observed, the enhanced corrosion rate observed in Salvadora, and Jatropha to some extent, may cause the fuel to go off-specification and requires a more thorough study.

3. Corrosion behavior of elastomers in biodiesel

An excellent review by Haseeb et al. [23] dealt with compatibility issues of automotive materials with biodiesel fuel. Biodiesel has been reported to cause corrosive as well as tribological wear on the metallic parts and elastomers in the engine. The tribological contact leads to removal of metal from the surface through abrasion, adhesion, corrosion, scuffing, and additive depletion. This causes mechanical damage to the surface of the metallic parts of the engine. Automobile engines have three major types of materials: ferrous alloys, non-ferrous alloys, and elastomers. The ferrous and non-ferrous metallic parts undergo corrosion through chemical/electrochemical attack and wear after coming into contact with biodiesel. A synergetic effect of corrosion and wear is thus caused in the metallic materials in contact with biodiesel. Ferrous alloys have better compatibility with biodiesel than non-ferrous ones. Copper alloys are more prone to corrosion than ferrous alloys. Fluorocarbons, a new group of compounds, have high resistance to corrosion. The extent of corrosion in biodiesel increases with the blend ratio and oxidation due to its contact with atmospheric oxygen.

Elastomers such as natural rubber, chloroprene/neoprene, and nitrile, are unsuitable for use in CI engines run on biodiesel. Haseeb et al. [36] did a SIT on three elastomers (nitrile rubber, polychloroprene, and fluoro-viton A) for compatibility with palm biodiesel at 25 and 50 °C for 500 h. The effect of biodiesel on corrosion was determined by measuring mass, volume, tensile strength, hardness, and elongation. Nitrile rubber and polychloroprene swelled and degraded in biodiesel; the reaction occurred between the polymer backbone and cross-linking system or with the filler system. However, the mass and volume of fluoro-viton A remained almost unchanged in biodiesel as well as diesel (Fig. 3). The absorption solvent and the relaxation of polymer chains increased mass and swelling of the nitrile rubber and polychloroprene. Increased cross-linking agent results in more swelling. In polychloroprene, glycol dimethacrylates present as cross-linking agent resulted in lower swelling in fuels compared to nitrile rubber. Swelling increased with increase in biodiesel content in the fuel. Elastomers include polar as well as non-polar substances. Thus, the polar end of the biodiesel (present in esters) interacts with the elastomers through dipole–dipole interaction, causing them to swell. This has been attributed to higher liquid absorption as compared to the extraction of soluble components from the elastomer. Increasing temperature had varying effect on elastomers. While increased swelling was observed in nitrile rubber, decreased swelling was observed in polychloroprene and almost no change was observed in fluoro-viton A at 50 °C. The reason attributed for loss in mass and volume in polychloroprene is its containing polychloroprene, which is stable at low temperature and thus its polar group gets dissolved in biodiesel, causing reduced weight and volume. A decrease in tensile strength was observed in nitrile rubber and polychloroprene. However, no change in tensile strength was observed in fluoro-viton. Analysis by FTIR spectrometry showed presence of carbon–carbon double bonds that may have resulted from reaction between the methylene or vinyl groups of nitrile rubber. The degradation of

nitrile rubber and polychloroprene in biodiesel has been attributed to the carboxylic polar groups present in biodiesel.

Haseeb et al. [37] tested the physical properties of various elastomers on their exposure to diesel and biodiesel (prepared from palm oil). The elastomers tested were ethylene propylene diene monomer (EPDM), silicone rubber (SR), polychloroprene (CR), polytetrafluroethylene (PTFE), and nitrile rubber (NBR). A SIT was carried out for B0, B10, B20, and B50 biodiesel at 25 °C for 1000 h. The physical properties of weight/volume loss, hardness, and tensile strength were determined after every 250 h of immersion. While biodiesel blends were found to cause high swelling in CR and NBR elastomers, the EPDM and SR elastomers swelled more in diesel than in biodiesel. PTFE elastomer showed slight loss in weight and volume, whereas other elastomers showed considerable gain in weight due to swelling. The reason attributed for high swelling in CR and NBR elastomers was the polar nature of the elastomers that dissolved in the biodiesel with its polar ester group. Exposure to metals may have caused oxidation of the fuel, which enhanced its polarity and further degraded the elastomers. When exposed to biodiesel, elastomers are affected in two ways: first by absorption of liquid by elastomers and second, by dissolution of soluble components from the elastomers in the liquid medium. Swelling was the result of high absorption amount by elastomers in comparison to their dissolution in the fuel. The tensile strength of biodiesel decreased to a large extent in the case of EPDM and CR. A minor decrease in tensile strength was observed in SR, PTFE and NBR elastomers. Among all of the elastomers, PTFE showed high compatibility with biodiesel that was attributed to absence in its polarity, although it also underwent reduction in its constituents. Swelling of the elastomers in biodiesel fuel can be retarded by adding cross-linking agents in the elastomers. Peroxides are commonly added as cross-linking agents [38].

4. Influence of water and microbes in the tank as causing agent for corrosion

Corrosion has been directly linked to presence of water in diesel storage tanks resulting from microbial growth in the tank. Bento and Gaylarde [39] reported the presence of anaerobic sulfate reducing bacteria in the diesel tank during long storage period (i.e., after 400 days). In the initial storage period, the aerobic bacteria (*Micrococcus*, oxidative gram negative rods, etc.) were detected (i.e., from the second day of storage), whereas yeast and filamentous fungi were detected from the ninth day. When left untreated, the bacterial colonies decreased substantially after 145 days which have been attributed to the increased acidity (pH = 3.5) during storage. The formation of colonies of anaerobic sulfate-reducing bacteria can be mitigated by inhibiting the formation of biomass at the oil/water interface. It was also found that the diesel storage tanks built in the ground are more prone to corrosion and when replaced by aerial system inclined at 30° to the horizontal facilitated the drainage of water, thus reducing the corrosion. Sørensen et al. [40] found that biodiesel was able to hold water around 20–30 times more than mineral diesel. The saturation level of water in the biodiesel was 1395 ppm as compared to 62 ppm in mineral diesel. Incubation of biodiesel (blend ratio with diesel ranging from B5, B10, B20, B50, and neat biodiesel) with water (from diesel storage tank) showed presence of both aerobic and anaerobic group of microorganisms such as methanogens, and sulfate- and nitrate-reducing bacteria in the aerobic rich (initial 84% aeration) fuel mixtures, thereby rendering the biodiesel to microbial degradation. Thus, corrosion can occur through both chemical corrosion and microbiologically influenced corrosion [40]. Wang et al. [41] studied the corrosion behavior of carbon steel in soybean biodiesel in the presence of tap water using a carbon steel beam electrode

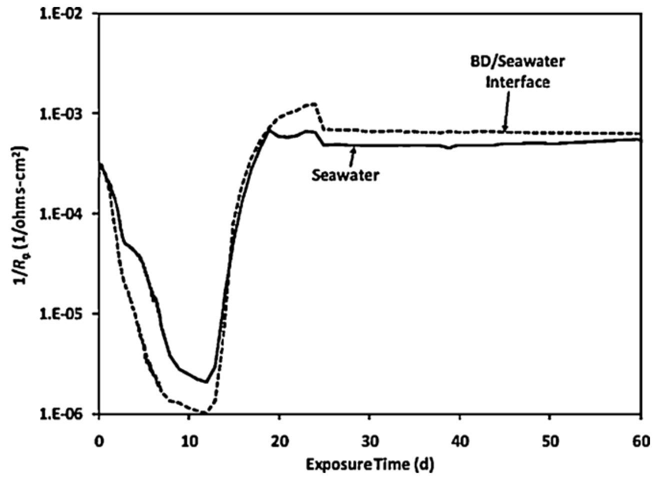


Fig. 4. Averaged $1/R_P$ instantaneous corrosion for coupons suspended in seawater and biodiesel/seawater interface [43].

(WBE). The WBE was positioned both horizontally and vertically in the storage tank. The electrode corroded with exposure to tap water added to the biodiesel. Twenty minutes after addition of water, cathodic currents formed on several wire electrodes along the edges of the water–biodiesel interface. When the time span was increased to 2 h, cathodic as well as anodic currents were detected. On increasing the time duration to 72 h, almost the entire electrode exposed to water was corroded, and rusting occurred by 120 h. As water solubility in biodiesel is very low (0.2%), water may form its way into the biodiesel container through condensation and may be in the suspended form between the biodiesel and metal surface interface. In addition, the water being insoluble and high in gravity will find its way to the bottom of the tank during stagnant conditions and, along with the impurities such as chloride in the biodiesel–water mixture, causes anodic and cathodic reaction at the metal surface. Cathodic reaction took place on the periphery of the water drop because of higher oxygen concentration compared to that in the bulk water. The anodic reaction, however, took place in the central part of the water drop due to high ion-promoted corrosion. Lee et al. [42] also reported highest tendency of biofouling on neat biodiesel and hence causing microbiologically influenced corrosion. Water is therefore found to promote microbial growth and thereby degrades the fuel.

Aktas et al. [43] reported that pitting corrosion was observed in carbon steel exposed to biodiesel that was subjected to anaerobic microbial decomposition in fresh and salt water. The carbon steel was tested for 60 days and analyzed with electrochemical and imaging techniques. The carbon strips in 3 sets were exposed in 3 different conditions: seawater immersion, seawater/biodiesel interface, and biodiesel immersion. The lighter biodiesel layer rose to the top of the seawater, where the polarization resistance (R_P) of the carbon strips was analyzed. The inversion of the polarization resistance ($1/R_P$) was reported to be proportional to the instantaneous corrosion rate. The first 10 days of exposure to the carbon steel in the biodiesel sample showed a decrease in corrosion rate from 5×10^{-4} to 10^{-6} $\Omega\,cm^{-2}$, which was attributed to the removal of oxygen. However, on the 12th day, corrosion rate started increasing, and increased to nearly 1×10^{-3} $\Omega\,cm^{-2}$ by the 18th day, after which it remained constant (Fig. 4). The $1/R_P$ value was slightly higher for the biodiesel/seawater interface compared to seawater.

The accelerated rate of corrosion of metals has been attributed to the formation of an acidic intermediate resulting from hydrolysis. This intermediate is then subjected to the process of β-oxidation. The half-life period for biodegradation of biodiesel has been reported to be less than 4 days at 17 °C [44]. Jayed et al. [45]

advocated for the necessity of a dedicated biofuel engine as severe corrosion, carbon deposition, and wearing of engine parts occurs during usage of biodiesel as fuel.

5. Corrosion in biodiesel storage container

Boonyongmaneerat et al. [46] correlated an important aspect of oxidation of biodiesel with corrosion. The oxidation of biodiesel occurs in several steps that leads to formation of primary products as well as secondary products. The primary products include hydroperoxides, whereas the secondary products include aldehydes, alcohols, formic acid, shorter chain carboxylic acids, and polymers. The shorter chain fatty acids further aggravate the acidity of biodiesel [47]. The presence of acidic chemicals causes corrosion inside the tank [48]. Biodiesel also has a strong tendency to absorb moisture from the atmosphere and undergo hydrolysis or hydrolytic oxidation. Oxidation of biodiesel or hydrolysis of the fuel causes degradation of biodiesel and corrosion of the steel-based container. Thus, the vicious circle begins, with corrosion further resulting in formation of sediments that get deposited on various engine parts such as injectors and pumps. The flow of the fuel to the engine is reduced, which results in a pressure drop across filters. Boonyongmaneerat et al. [46] studied the effect of nickel (NiW-1) and two nickel–tungsten (NiW-2) alloys as electrodepositing metals for coating in steel-based biodiesel containers for a 3-month duration. Loading amounts of tungsten on the nickel were 44 and 39%, respectively. Pure nickel metal was found to offer a high corrosion resistance to biodiesel and its vapors during the SIT. The nickel–tungsten alloy showed high occurrence of corrosion in just 1–2 months. After 3 months, water content of biodiesel increased from 700 to 1800 ppm, which was indicative of the water absorption capacity of biodiesel. However, the acid value increased from just 0.8 to 1.1 mg KOH/g in the 2-month period. The bare steel was highly prone to corrosion owing to degradation of the fuel through oxidation and hydrolysis. Corrosion was prominent at slightly above and below the air–biodiesel interface of the specimen strip dipped in biodiesel. An important observation was occurrence of corrosion in the air-exposed portion of the NiW-1 strip in only a 1-month period. After the long-term immersion, $\sim$3 and 4 wt% of nickel were found to be dissolved from NiW-1 and NiW-2 specimens, respectively, whereas tungsten remained almost constant.

6. Corrosion inhibitors for metals bearing contact with biodiesel

Corrosion inhibitors may be added to retard the corrosion of metallic parts by biodiesel [49,50]. The common corrosion inhibitors used in oil and gas are imidazolines, primary amines, diamines, amino-amines, oxyalkylated amines, naphthaneic acid, phosphate esters, and dodecyl benzene sulfonic [51]. The compounds used as inhibitors in diesel include carboxylic acids, amines, and amine salts of carboxylic acids such as alkyl- or polyalkylsuccinics and their esters, dimeric acids, and amine-salts [52]. However, the composition of biodiesel (i.e., mono-alkyl esters of fatty acids) is different from that of mineral diesel (i.e., hydrocarbons). The type of corrosion inhibitors will be different for these two fuels. It is also important to remember that inhibitors cannot prevent corrosion, but only extend the time before corrosion starts to occur in the metallic parts exposed to biodiesel [53].

The auto-oxidation of biodiesel can enhance the corrosiveness of biodiesel. Fazal et al. [54] investigated the inhibitory efficiency of amine-based corrosion inhibitors ethylenediamine (EDA), n-butylamine (nBA), and tert-butylamine (TBA) against corrosion of cast iron in SIT. Cast iron is widely used in the manufacturing of automotive components such as pistons, piston rings, cylinder liners, and exhaust systems [9]. The effectiveness of the inhibitors was in the following order: EDA > TBA > nBA. The SIT was performed for 1200 h (50 days) and was found to be 0.0771 mpy for grey cast iron of the composition: C, 3%; Si, 1.84%; P, 0.098%; S,0.089%, and the remaining part being iron. The analysis on the XRD peaks showed the formation of oxides: FeO and Fe_2O_3. With the addition of TBA in biodiesel, a new phase $\{Fe(NO_3)_3{\cdot}9H_2O\}$ was formed. The corroded samples also showed the formation of sediments that can further deteriorate the fuel properties by causing problems such as engine choking, moving parts sticking, filter plugging, etc. The mechanism of the inhibitors was the stable metal oxide layer formed on the surface of the metal exposed to biodiesel. The amine-based inhibitors are thus absorbed on the surface of the metal and prevent corrosion by forming a barrier. Li et al. [55] reported that amine-based inhibitors protect corrosion through adsorption onto the metal surface. Adsorption occurs either through metal–nitrogen bonding via pi electrons by chemisorptions, or with a protonated amine by the formation of a hydrogen bond to the metal surface. Among the inhibitors, TBA imparted no color or sediment when added to the biodiesel. EDA, however, caused the formation of sediments changing color from white to light yellow; nBA also caused a minor change in color. The formation of the sediment on addition of EDA has been attributed to the formation of diamine which is formed from the reaction of acid and esters in biodiesel. The presence of amide was also confirmed by occurrence of spectra at 3300 cm^{-1}, 1550, and 1640 cm^{-1}.

Almeida et al. [56] tested the effect of antioxidants, *tert*-butylhydroquinone (TBHQ), and the correlation of oxidation stability and corrosion on copper coupons through the SIT. The oxidation stability test was done by induction rancimat method. The TBHQ retarded the corrosiveness of the copper release and retarded corrosion when added to biodiesel by adsorbing at the copper surface and being catalytically oxidized to tert-butylquinone (TBQ). The presence of the antioxidant resulted in the decrease in the induction time of biodiesel fuel from 24 h to 2.42 h under copper immersion corrosion test. The copper concentration in the fuel increased more in the absence of TBHQ; its concentration was negligible until 50 h when it increased to 1.16 $\mu g\, g^{-1}$, while in the neat biodiesel, the concentration rose to 3.62 $\mu g\, g^{-1}$. The mechanism reported for the TBHQ is the formation of a protective film layer on the copper coupon. TBHQ was also consumed, further strengthening the hypothesis of its functioning as a corrosion inhibitor.

7. Conclusion

Currently designed engines use gasoline or petrodiesel as fuel. Alternative fuels such as biodiesel raise the issue of corrosion in CI engine parts that come into contact with the fuel. This review demonstrates that corrosion is higher with biodiesel than petrodiesel fuel. The rate of corrosion is influenced by temperature, water content, microbial growth, and type of feedstock used for synthesis of biodiesel. Feedstock with higher concentrations of unsaturated fatty acids has greater oxidation rates. The commonly employed metals such as aluminum, copper, copper alloys, and steel to some extent, were found to be prone to corrosion. Pitting corrosion has been common in the metals that have been tested for their corrosiveness in biodiesel. However, stainless steel was found to be immune to pitting corrosion. Corrosion was found to cause swelling in the elastomers. The polar nature of the elastomers dissolved in the biodiesel caused the corrosion.

Corrosion of metallic parts and elastomers takes a long duration. Current studies done on metal samples commonly used in CI engines have been done for a limited period of time (1000 h or 300 days). Further testing carried out for longer durations is needed to

provide a better understanding of corrosion for application. A few inhibitors (ethylenediamine, tert-butylamine, and n-butylamine) have been found to be effective in the formation of a stable metal oxide as protective layer and thus retarding corrosion in biodiesel. An antioxidant, *tert*-butylhydroquinone, was also found to retard the corrosion of copper coupon in biodiesel along with enhancing the oxidation stability of the fuel. Further studies on the effectiveness of inhibitors added to biodiesel are needed.

Acknowledgment

One of the author, Bhaskar Singh is thankful to CSIR, New Delhi, India for grant of prestigious “Research Associateship”.

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